Deprotection, Tethering, and Activation of a Catalytically Active Metalloporphyrin to a Chemically Active Metal Surface: [SAc]₄P−Mn(III)Cl on Ag(100)

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Received September 26, 2008; E-mail: rml1@cam.ac.uk

Abstract: The adsorption and subsequent thermal chemistry of the acetyl-protected manganese porphyrin, [SAc]₄P−Mn(III)Cl on Ag(100) have been studied by high resolution XPS and temperature-programmed desorption. The deprotection event, leading to formation of the covalently bound thioporphyrin, has been characterized and the conditions necessary for removal of the axial chlorine ligand have been determined, thus establishing a methodology for creating tethered activated species that could serve as catalytic sites for delicate oxidation reactions. Surface-mediated acetyl deprotection occurs at 298 K, at which temperature porphyrin diffusion is limited. At temperatures above ∼425 K porphyrin desorption, diffusion and deprotection occur and at >470 K the axial chlorine is removed.

Introduction

The bottom-up fabrication of systems consisting of functional molecules tethered to solid surfaces is an important research area of relevance to a wide range of applications including electrochemistry, molecular electronics, and catalysis.[1] Robust, reproducible molecule-surface tethering is important and is often achieved by means of thiol linkages. However, the reactivity of thiol groups is such that they need to be protected during synthetic procedures and then deprotected to enable covalent linkage to the solid surface. Recent interest in the electrochemical and physical properties of metalloporphyrins has stimulated work on the covalent attachment of these macrocycles to electroactive surfaces, an important example being the synthesis of thiol-functionalized porphyrins,[2−10] led by the work of Lindsey et al.[3] Our interest lies in a hitherto neglected field: the attachment of catalytically active metalloporphyrins to metal surfaces to create hybrid catalytic systems in which the characteristic chemistry of the porphyrin is harnessed to the complementary chemistry of the metal surface, for example to produce systems capable of carrying out delicate selective oxidations. We choose silver because at ambient temperature it can dissociatively adsorb dioxyen and π-adsorb alkenes, thus preparing the reactants in the desired state.

We have previously made a porphyrin-functionalized silver surface that exhibits ligand binding, unbinding, and displacement reactions characteristic of the free metalloporphyrin[11] and have also used well-chosen ligands to dramatically alter their dynamics.[12] Such weakly bound systems are unlikely to be sufficiently robust for catalytic applications, however, especially in the presence of a solvent where resistance to leaching is an essential attribute.

Very recently, we reported the first direct observation by scanning tunneling microscopy (STM) of *spontaneous* surface-mediated deprotection of a *free base* thiol-terminated porphyrin ([SAc]₄P−H₂) on Ag(100):[13] such tethered porphyrins possess no inherent catalytic properties, of course. Here we extend this work into the domain of chemically active metalloporphyrins that are known to catalyze oxygen transfer reactions in

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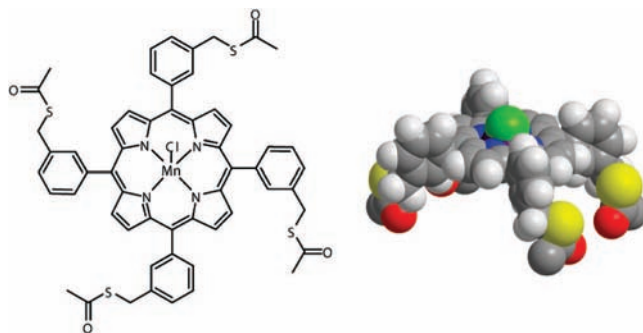
Figure 1. Molecular structure and 3D space-filling model of [SAc]₄P−Mn(III)Cl.
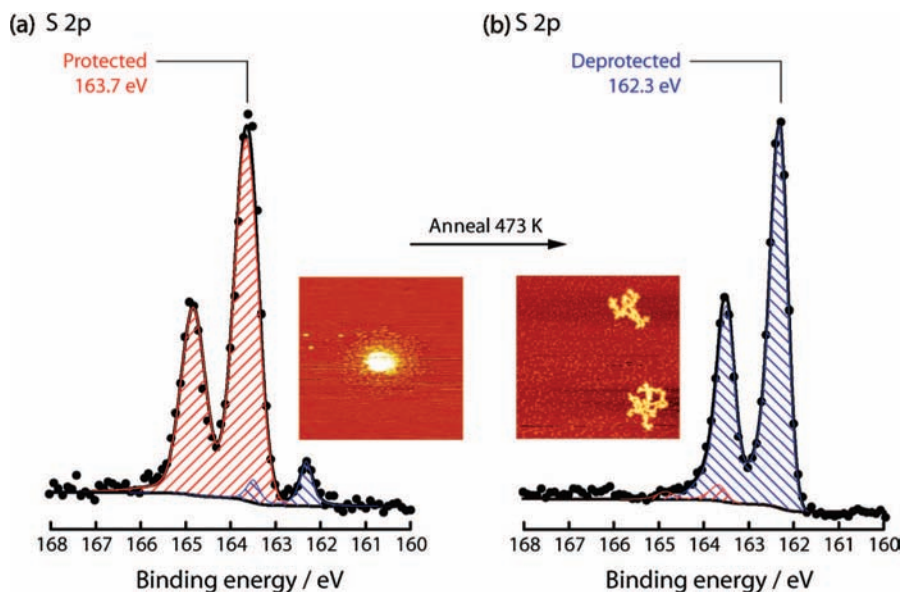
Figure 2. S 2p region of XP spectra acquired (a) immediately following porphyrin deposition and (b) after subsequent annealing at 473 K. As a guide, the XP spectra are overlaid with a representative STM image of an equivalent surface state for the free base porphyrin, [SAc]₄P—H₂, taken from ref 13 (left image: 900 Å × 900 Å, V_{tip} = 1.5 V, I = 0.1 nA; right image: 400 Å × 400 Å, V_{tip} = 0.75 V, I = 0.05 nA).
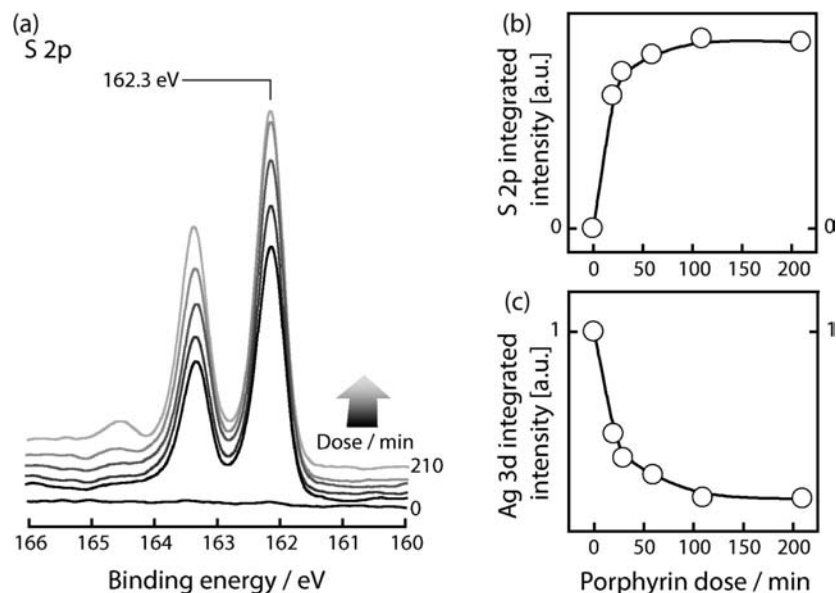

Figure 3. (a) S 2p region of XP spectra taken with increasing [SAc]₄P—Mn(III)Cl porphyrin dose time. In each case the surface was annealed at 473 K for 15 min prior to recording the spectrum. (b) Integrated S 2p intensity for each curve, plotted with respect to porphyrin dose time. (c) Associated Ag 3d integrated intensities.

solution.[14−21] As explained above, this is the next step toward the creation of hybrid heterogeneous selective oxidation catalysts. Our aim was to deposit the acetyl-protected porphyrin [SAc]₄P—Mn(III)Cl (Figure 1) on Ag(100), deprotect it by removal of the acetyl groups thus enabling covalent tethering to the surface by Ag—S bonds, and finally activate it by removal of the axial chlorine ligand. The actual sequence of events was followed under well-defined conditions by means of synchrotron high-resolution X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). In regard to their homogeneous chemistry, manganese porphyrins are well-known for their effectiveness as selective oxidation catalysts when used in conjunction with a single-oxygen donor.[14−21] In the present

case, the silver surface bearing oxygen adatoms is envisaged as the entity that will act the single-oxygen donor.

Experimental Methods

The free base 5,10,15,20-tetrakis[3-(S-acetylthiomethyl)phenyl]porphyrin was synthesized using the method described by Lindsay et al.[3] Metalation of the free-base porphyrin was achieved in a mixture of acetic acid:acetic anhydride = 4:1 at 110 °C using MnCl₂·4H₂O as the manganese source. After completion of the reaction, the remaining inorganic salts were filtered, leaving the pure [SAc]₄P—Mn(III)Cl porphyrin.

High resolution XPS was carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation source in Trieste, Italy. Spectra were collected using a single-pass 32-channel concentric hemispherical electron analyzer, and the angle between the entrance
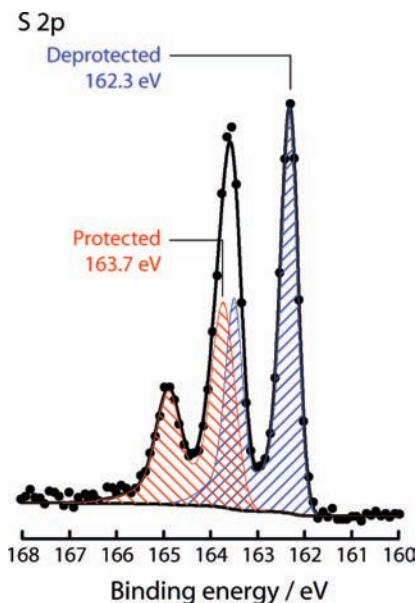
Figure 4. S 2p region of the XP spectrum acquired after initial deposition and following 10 h left at room temperature. The protected S contribution is represented by red hatching; deprotected S is represented by blue hatching.

lens of the analyzer and the incoming photon beam was 70° in the horizontal plane. Experiments were performed with a photon incidence angle of 10° with respect to the surface. The Ag(100) crystal was attached to a motorized manipulator via a tantalum backplate fitted with a T1T2 thermocouple and could be heated resistively to 900 K or cooled to 77 K. Repeated cycles of Ar^+ (99.999% Messer) sputtering followed by annealing at 800 K were carried out until a clean, atomically flat surface was obtained, as monitored by XPS and LEED.

Temperature-programmed desorption experiments were conducted in Cambridge in an ultrahigh vacuum chamber operated at a base pressure of 1×10^{-10} torr. The sample was exposed to gases by backfilling the chamber which was equipped with an Omicron 3 grid retarding field analyzer for LEED/AES analysis and a VG 300 quadrupole mass spectrometer whose ionizer was positioned 5 mm from the front face of the sample. The Ag(100) single crystal could be cooled to 100 K and heated to 1400 K, monitored by a T1T2 thermocouple attached directly to the sample. The sample was cleaned by repeated cycles of Ar^+ (99.999% Messer) sputtering followed by annealing at 700 K until a clean atomically flat surface was obtained, as observed by LEED and AES.

Porphyrins were deposited onto the Ag surface, both in Cambridge and in Trieste, by means of a resistively heated collimated evaporation source fitted with a T1T2 thermocouple. The (very small) amounts of porphyrin used were injected into the sublimation source as solutions in dichloromethane which were evaporated to dryness before mounting in the vacuum chamber.

Results and Discussion

Figure 2a shows the S 2p spectrum acquired following initial deposition of the porphyrin with the Ag(100) sample at 300 K. Three peaks are clearly evident which are due to two distinct, overlapping S 2p$_{1/2,3/2}$ doublets. The emission at higher binding energy of 163.7 eV (red hatching) is due to thiol groups that are still acetyl protected. The component at lower binding energy, centered at 162.3 eV (blue hatching), may be confidently assigned[22] to *deprotected* thiol groups covalently bonded to the silver surface, after cleavage of the acetyl group.

Annealing at 473 K for 15 min resulted in the XP spectrum shown in Figure 2b. Note that this procedure is the same as
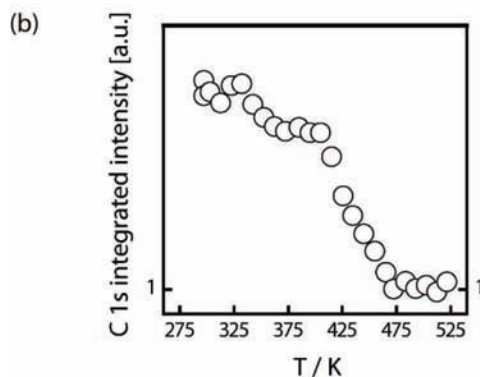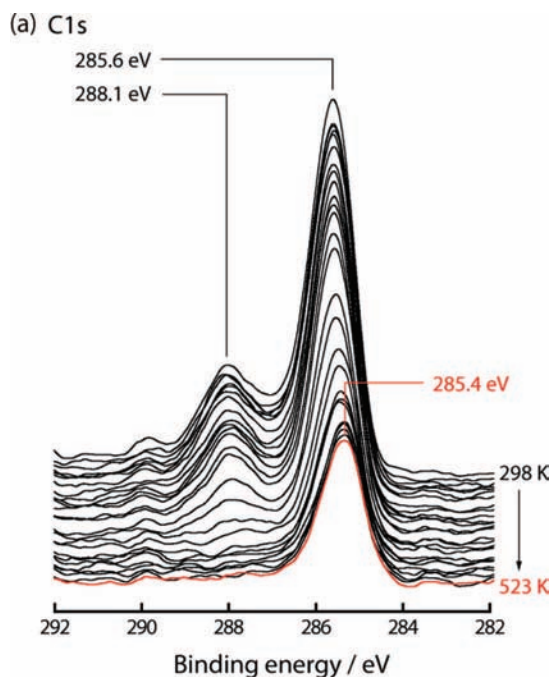

Figure 5. (a) C 1s region of the temperature-programmed XP spectrum acquired while applying a 5 K s^{-1} temperature ramp from 298 to 523 K. (b) C 1s integrated intensity of each curve plotted with respect to temperature.
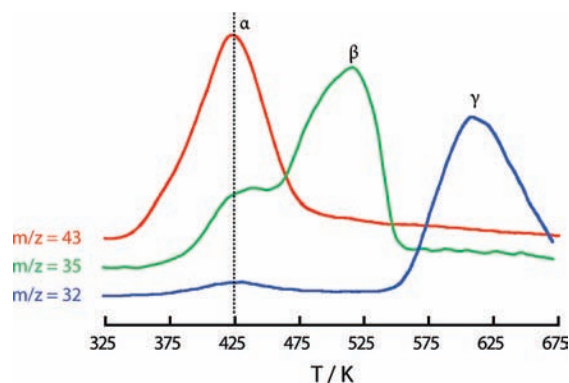

Figure 6. Temperature-programmed desorption data acquired after dosing [SAc]$_4$P−Mn(III)Cl onto clean Ag(100). Curves correspond to: $m/z = 43$ (CH_3CO^+), $m/z = 35$ (Cl^+), $m/z = 32$ (S^+).

that used for dispersing and deprotecting the closely related *free base* porphyrin [SAc]$_4$P−H$_2$ where we were able to follow the surface processes by means of STM.[13] In that case, verification of the expected ratio of cleaved acetyl groups to deprotected porphyrin molecules was possible: in the present case the C 1s
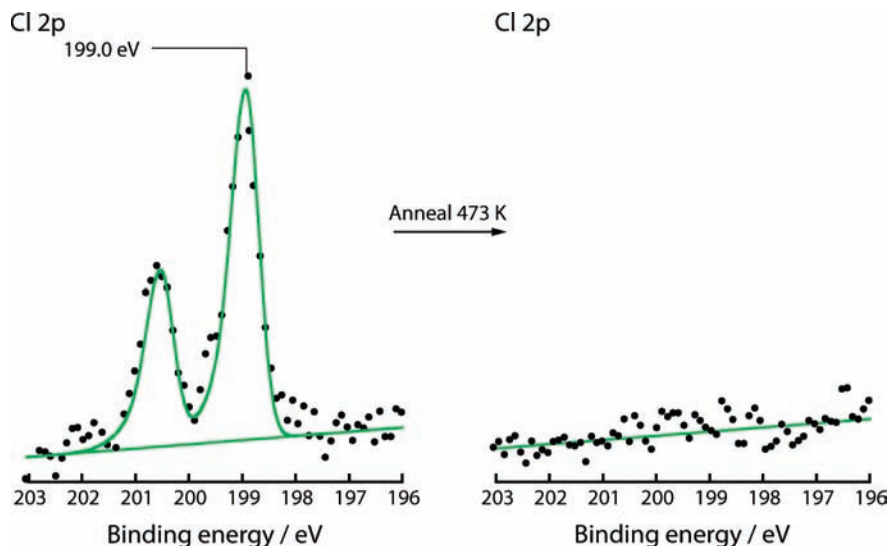
Figure 7. Cl 2p XP spectrum acquired after initial deposition of [SAc]₄P−Mn(III)Cl (left) and after subsequent annealing at 473 K for 15 min (right).
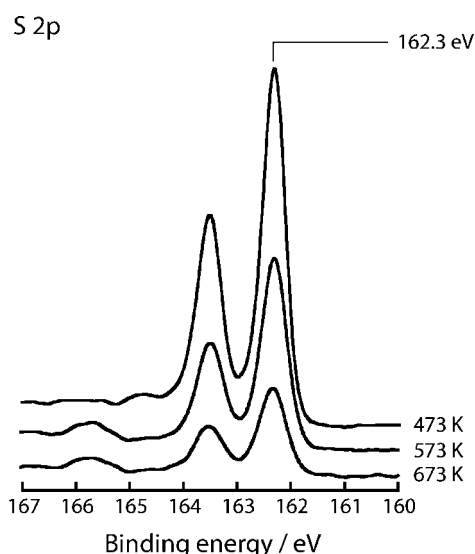

Figure 8. S 2p emission as a function of thermal treatment: spectra acquired after annealing the porphyrin-covered surface to the indicated temperature for 5 min.

emission does not distinguish between the acetyl carbon atoms and macrocycle carbon atoms. For the purpose of illustration, the corresponding images taken from ref 13 are shown as insets to Figure 2. It is apparent from Figure 2b that 473 K annealing leads to essentially complete deprotection of remaining porphyrin. The presence of a single S 2p signal clearly indicates that all thiol groups are bonded to the silver surface.

Figure 3a shows the uptake of [SAc]₄P−Mn(III)Cl as monitored by the S 2p emission; the right panel shows a plot of corresponding integrated intensities of the S 2p and Ag 3d emission as a function of dosing time. These data were acquired by depositing the porphyrin at room temperature followed by annealing at 473 K for 15 min to disperse the initially formed 2D islands and desorb any multilayer material, a process that occurred at ∼425 K (see below): this deposition method provided a convenient way of preparing any given coverage in the submonolayer to monolayer regime. The procedure was then repeated in order to build up coverage from the submonolayer regime to that of a fully saturated covalently bonded monolayer. (The weak Cl 2p emission and the undetectability of Mn 2p

emission are consistent with the low number density of Cl and Mn atoms on the surface even at saturation coverage, even though both were examined at the optimum photon energies that maximized the photoionozation cross sections: Cl 2p = 3 Mb, Mn 2p = 1 Mb.[23])

It is apparent from Figure 2 that at room temperature a small degree of thiol deprotection occurs immediately upon deposition. This implies that cleavage of acetyl groups is surface-mediated and that the process is limited by the inability of most porphyrin molecules to access the surface as suggested by the inset to Figure 2a (i.e., the relevant STM image): the majority are present in large aggregates, and only those at the periphery can undergo deprotection. Elevated temperatures increase porphyrin diffusion and deprotection (Figure 2), although even at room temperature, given sufficient time, a significant degree of deprotection occurs. Figure 4 illustrates a S 2p XP spectrum acquired 10 h after initial S deposition; the situation is intermediate between the two extreme cases of total protection/deprotection shown in Figure 2.

Figure 5a shows a series of temperature-programmed C 1s XP spectra acquired over the interval 298 K to 523 K with a ramp rate of 5 K s⁻¹, after deposition of [SAc]₄P−Mn(III)Cl. Upon porphyrin deposition, two C 1s signals

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were observed at 285.6 and 288.1 eV. Upon raising the temperature, the 288.1 eV component attenuated rapidly, disappearing by 523 K, at which point only the lower binding energy component remained, slightly downshifted to 285.4 eV. These two components are ascribed, respectively, to porphyrin molecules in contact with the Ag surface (285.6 eV) and molecules in the second or higher layers (288.1 eV), the lower binding energy of the former reflecting greater final state screening of the C 1s core hole by the Ag valence electrons.[24]

Figure 5b, showing the total integrated C 1s intensity as a function of temperature, is consistent with this interpretation. The initial slow decrease in the C 1s integrated intensity is principally due to evaporation of the more weakly held "multilayer" molecules, followed by a much faster decrease that sets in at 410 K due to desorption of molecules in the contact layer. The limiting C 1s intensity at 523 K decreased by a further ~10% upon heating to 573 K.

Representative TPD measurements carried out after deposition of [SAc]$_4$P−Mn(III)Cl on Ag(100) are shown in Figure 6 for $m/z = 43$ (CH$_3$CO$^+$), $m/z = 35$ (Cl$^+$), $m/z = 32$ (S$^+$), the three data sets being acquired simultaneously; m/z values >100 were beyond the range of the quadrupole mass spectrometer. The maximum at 425 K in the $m/z = 43$ profile is assigned to the CH$_3$CO$^+$ fragment ion due to protected porphyrin molecules desorbing from the contact layer ($m/z = 43$ was an intense signal in the mass spectrum of the porhyrin vapor from the evaporation source). This is in good agreement with the XPS results (Figure 5b) which exhibit a steep decline in C 1s intensity over the same temperature range. The TPD result also implies that upon raising the temperature some of the acetyl-protected molecules desorb intact, whereas others undergo deprotection and become strongly bound to the surface via S−Ag linkages. Correspondingly, the coincident feature at 425 K in the $m/z = 35$ spectrum is assigned to the Cl$^+$ fragment ion from intact desorbing porphyrin molecules.

The Cl$^+$ desorption peak at ~515 K corresponds to loss of the manganese-bound chlorine ligand, and in this connection the XPS results illustrated in Figure 7 are revealing. Examination of the Cl 2p emission before and after annealing the porphyrin layer at 473 K (onset of chlorine loss in Figure 6) for 15 min shows complete removal of Cl from the surface. It is well-known that Cl chemisorbs strongly on silver surfaces forming AgCl[25] which acts to assist porphyrin dechlorination during the relatively mild thermal treatment. This process both deprotects and immobilizes the porphyrin *and* leaves the manganese metal center in a low-coordination state, thus preparing it as a catalytically active site.

At temperatures above ~560 K the deprotected porphyrin molecules decompose with desorption of sulfur (Figures 6, 8) and formation of a carbonaceous residue (Figure 5a,b). The S 2p intensity that persists after heating to 673 K (Figure 8) is consistent with Figure 6 from which it is apparent that S desorption is incomplete at this temperature.

Conclusions

The acetyl-protected manganese porphyrin, [SAc]$_4$P−Mn (III)Cl may be deposited on Ag(100) and subsequently deprotected, leading to stable, covalently bound thioporphyrin molecules. These in turn may be dechlorinated, resulting in formation of stable, surface-tethered low-coordinate Mn centers, thus establishing a methodology for creating thio-tethered activated species that could serve as catalytic sites for delicate oxidation reaction. These species appear to be stable to over 500 K which is well above the temperature range of the intended application.

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